Recovery of glucose and polyester from textile waste by enzymatic hydrolysis

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Abstract

In order to recover glucose and polyester from textile waste, enzymatic hydrolysis of textile waste pretreated by different modification methods was investigated. The effects of key factors related to hydrolysis process were evaluated, including substrate loading, temperature, pH, cellulase dosage, and supplementation of β-glucosidase. Results showed that freezing NaOH/urea could contribute to significant increase of the hydrolysis yield compared with untreated textile waste, from 57.7% to 98.3%. Increasing substrate loading from 1% to 7% (w/v) had a negative effect on glucose recovery yield and significant inhibitory effect was observed over 3% substrate loading. Substrate loading at 3% was selected based on glucose yield. The optimal temperature for enzymatic hydrolysis was 50 °C and significant reduction was observed over 60 °C. There was no significant increase of glucose recovery yield observed when cellulase loading was over 20 FPU/g and β-glucosidase loading was over 10 U/g. Therefore, the optimum enzymatic hydrolysis condition was using 20 FPU/g cellulase and 10 U/g β-glucosidase at 50 °C and pH 5, based on the criterion for minimizing enzyme dosage and maximizing glucose recovery. The maximum glucose recovery yield of 98.3% was achieved after 96 h hydrolysis.

Keywords: Enzymatic hydrolysis, Glucose recovery, Polyester recycling, Textile waste

Abbreviations

ANOVA: Analysis of Variance

DSC: Differential Scanning Calorimetry

FTIR: Fourier Transform Infrared Spectrophotometer

NMMO: N-methylmorpholine-N-oxide

PET: Polyethylene terephthalate (Polyester)

SEM: Scanning Electron Microscopy

1. Introduction

In recent years, there has been an increasing concern in the management of textile waste. The worldwide consumption of textile fibers was over 96 million tonnes in 2016 and it was forecasted to keep increasing due to population growth and the rise of purchasing power [1]. The fast growth of textile production has resulted in a considerable amount of textile waste, of which annual generation in China, the United States and the United Kingdom is estimated to be 26.0, 15.1, 1.7 million tonnes, respectively [1]. Textile waste is categorized into two groups, pre-consumer textile waste and post-consumer textile. The major component of pre-consumer textile waste is raw textile fibers including protein fibers, cellulosic fibers and synthetic fibers [2,3]. Textile waste generated during the constant usage and disposal is classified as post-consumer textile. Currently, the main textile waste management methods are recycling by donation, combustion with energy recovery and landfilling [4]. Around 64.5% of textile waste ended up in landfills in the United States in 2015 [4]. In Hong Kong, the amount of textile waste generated was 343 tonnes per day in 2016 [5]. The majority of textile waste was disposed at landfills, up to 96.6% [5]. Textile waste disposal at landfills exerts more pressure on the limited landfill space, since relatively long time (from 6 months to 20 years) is required for textile decomposition related to different types of fabrics and environment of landfill [6]. As for incineration, there is a high chance to generate toxic compounds such as dioxin during high temperature combustion, which can accumulate in food chain and have a highly toxic potential to

human beings' heath [7]. In recent years, a growing trend towards the aim of textile waste to value-added products emerged as number of publications in the valorization of textile waste increases. Keywords such as 'textile waste valorization', 'textile waste hydrolysis' and 'textile waste recycling' were searched in ScienceDirect database from 2012 to 2017. As shown in Fig. 1, results indicate that there has been an upward trend in the number of publications focused on textile waste in the past five years. It should be pointed out that the biological concept, 'textile waste hydrolysis', was always considered together with textile waste recycling. Therefore, it is necessary to investigate an environmentally and economically sustainable process to recycle textile waste.

Cotton is one of most commonly used textile fibers, in which cellulose content is up to 99% after industrial treatment. Consequently, cotton content in textile waste is mainly considered as an alternative source for the production of renewable energy, and it has been investigated as a feedstock in the bioprocess of bioethanol biorefinery [8-11] and biogas production [9,10]. During biological process via enzymatic hydrolysis, catalytic reaction can occur when cellulase binds with cellulose on specific site [2]. However, cotton-based textile is commonly blended with different ratios of polyester and its well-organized blending structure can obstruct enzymes from accessing the cotton. Another problem is that cotton has relatively higher crystallinity and degree of polymerization, which results from high molecular weight as well as inter- and intra-molecular bonds [12]. Current research mainly focuses on pretreatment methods to facilitate access of enzymes to internal structure of cellulose.

Shen et al. developed a potentially profitable process for sugar and polyester recovery from cotton-based textile wastes via H_3PO_4 treatment. The maximal sugar recovery yield of 79.2% was obtained after 85% phosphoric acid treatment for 7 h at 50 °C [13]. Alkaline pretreatment was also investigated to enhance the glucose and ethanol yield from polyester/cotton blended textile. Over 88% of enzymatic hydrolysis yield was obtained after the pretreatment with NaOH/urea [8]. Jeihanipour et al. used an environmentally-friendly cellulose solvent, N-methylmorpholine-N-oxide (NMMO), to pretreat textile waste for enhancement of ethanol and biogas production [10]. For cotton-based ethanol production, efficient saccharification is of great importance and contributes to higher concentration of ethanol. Relatively lower enzyme input in hydrolysis was also suggested in previous techno-economic evaluations [14,15].

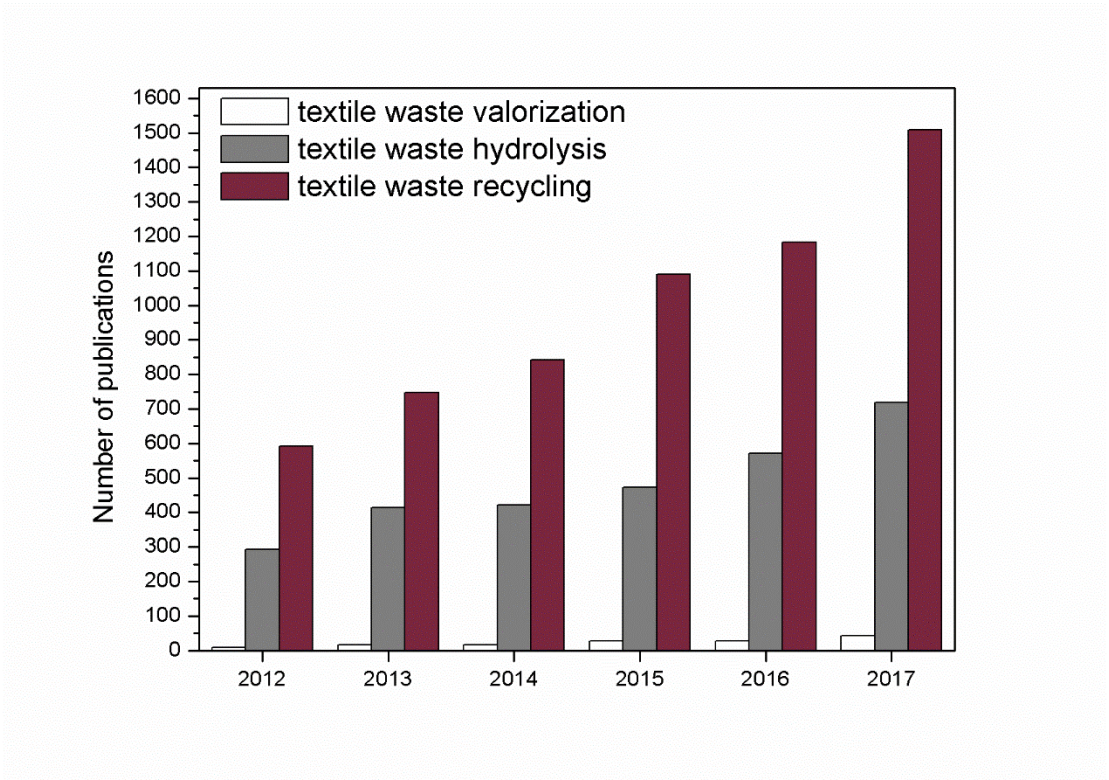


Fig. 1 The increasing trend of publications about textile waste treatment based on

ScienceDirect database from 2012 to 2017

In this work, we aimed to investigate the optimal conditions for enzymatic hydrolysis and recycling of textile waste with the lowest energy and enzyme inputs. The key factors related to hydrolysis were investigated in this study, such as substrate loading, temperature and pH. Regarding enzyme inputs, the dosages of cellulase and β-glucosidase were also investigated.

2. Materials and methods

2.1 Substrates and enzymes

Textile waste blending of cotton and polyester (PET) by 60/40 from H&M manufacturing plants in China was employed as raw material, in which blue reactive dye stuff was used. The crude textile fabrics were grinded into small pieces (size approximately 1×1 cm^2) by the grinder WSM-D200X160 (OMS Machinery Co. Ltd., Zhongshan, China) prior to pretreatment.

Two types of commercial enzymes were used in this study, cellulase (Celluclast 1.5L, Novozymes, China) and β-glucosidase (Sunson, China). The activity of cellulase was 75 FPU/mL, determined by Adney and Baker method [16]. The activity of β-glucosidase was measured as 9,000 U/mL by Herr Method [17].

2.2 Textile pretreatment

Two types of modification methods were investigated in this work, including freezing

NaOH/urea and milling. For freezing NaOH/urea method, textile waste was soaked in the alkaline mixture of 7 w/v% sodium hydroxide and 12 w/v% urea at -20 °C for 6 h. The solid loading for textile pretreatment was 5% (w/v%). The pretreated samples were washed by tap water until pH 7 to remove alkaline residues, then dried in an oven at 60 ºC for 48 h. As for the milling pretreatment, textile waste was milled by a hammer crusher, into powder form with a diameter of less than 1 mm.

2.3 Enzymatic hydrolysis

Textile fabrics were enzymatically hydrolyzed in 50 mM sodium citrate buffer (pH 5.1) in 250 mL Duran bottles with 100 mL working volume. Different substrate loadings (1-7 w/v %), cellulase (10-40 FPU/g) and β-glucosidase (0-50 U/g) dosages were used. The dosage of enzyme was calculated based on the dry weight of textile waste. The hydrolysis was performed at 50 °C in water bath at 350 rpm using magnetic stirring bar for 96 h. Samples were taken at different time points (0 h, 3 h, 6 h, 9 h, 12 h, 24 h, 48 h, 72 h, 96 h) during the hydrolysis process. After centrifugation at 10,000 rpm for 3 min, the supernatant was collected and stored at -20 ºC for further sugar analysis. All hydrolysis experiments were carried out in duplicate. The glucose yield was calculated using Eq.1 [8].

$$\text{Glucose yield} = \frac{\text{Amount of glucose released}}{\text{Initial amount of cellulose} \times 1.11} \times 100\% \qquad \text{Eq.1}$$

2.4 Analytical methods

Determination of glucose concentration was conducted by HPLC (Waters, Milford, USA), which was equipped with a RI detector (Waters 2414). Glucose was analyzed

155 using an Aminex HPX-87H column (Bio-Rad, USA) at 60 °C with 0.6 mL/min eluent
156 of 5 mM sulfuric acid.

157 2.5 Microscopic Observation and Scanning Electron Microscope Detection

158 The textile substrates were observed at a magnification of ×400 by a microscope
159 (Keyence, VHX-2000). Images of textile structure before and after enzymatic
160 hydrolysis were also taken by Scanning Electron Microscope (SEM) at a
161 magnification of ×300 and voltage of 20 kV using a Germany SEM (Carl Zeiss EVO
162 10).

163 2.6 Statistical analysis

164 All data were processed by IBM SPSS software (version 22.0), and the hydrolysis
165 results at different conditions were compared using one-way Analysis of variance
166 (ANOVA). The significant differences among the different conditions were
167 determined by Duncan multiple range test and significant P-value was obtained after
168 statistical analysis.

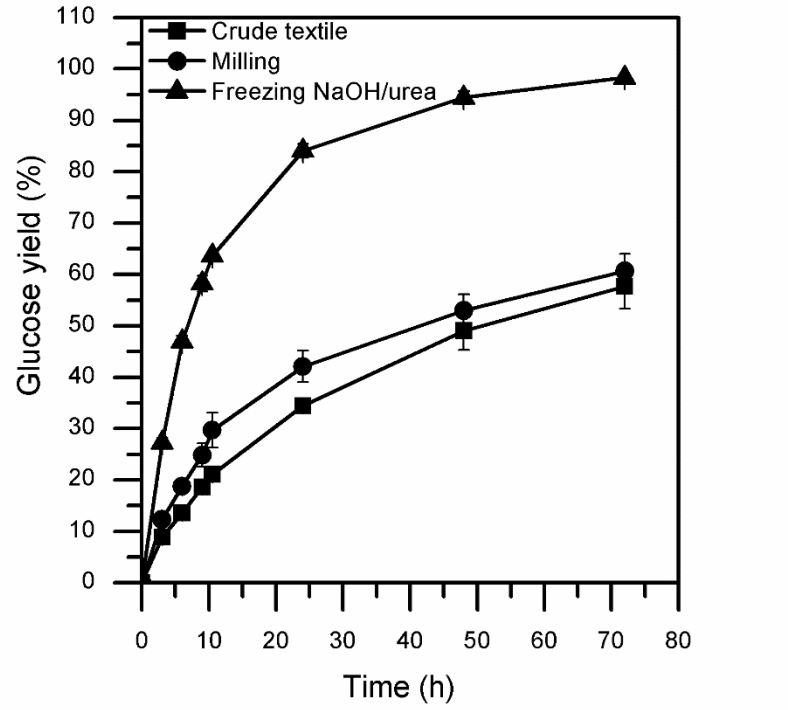
169 **3. Results and discussion**

170 3.1 Sugar recovery of textile fiber after different modification methods

171 The highly organized crystalline structure of cellulose in cotton fiber is the main
172 obstacle to improve the bioconversion rate. An effective modification method is
173 crucial to enhance sugar recovery yield [8,9,13]. In order to investigate the proper
174 modification method to pretreat textile waste, comparison of different pretreatment

was conducted. Prior to enzymatic hydrolysis, textile waste blending of cotton and PET by 60/40 was subjected to two types of modification methods: (i) freezing NaOH/urea, and (ii) milling. After pretreatment, crude textile, freezing NaOH/urea pretreated textile and milled textile were subjected to enzymatic hydrolysis for 72 h at 3% of substrate loadings with 30 FPU/g cellulase and 300 U/g β-glucosidase. The results of enzymatic hydrolysis were presented in Fig. 2. The glucose yields after 72 h enzymatic hydrolysis from crude textile, freezing NaOH/urea pretreatment and milling were 57.7%, 98.3% and 60.6%, respectively. The freezing NaOH/urea pretreatment contributed to a significant enhancement ($p<0.05$) of the final glucose yield, from 57.7% to 98.3%. As shown in Fig. 2, two stages in cellulose-glucose conversion were observed. Most of glucose recovered from cotton fibers occurred within the early 24 h, followed by a slow enzymatic hydrolysis reaction. There was only a slightly increase of glucose yield after 48h. The high efficiency in the first 24h could be attributed to textile structural modification by alkaline pretreatment, which destroys inter- and intra-hydrogen bonds between cellulose molecules and thus reduces cellulose crystallinity [18]. The obtained results are consistent with that from other types of blended textile fibers and alkaline pretreated spruce [8,19]. As for the milling pretreatment, the increase of glucose yield was only 2.9% ($p>0.05$) as compared with crude textile, although accessible surface area was increased after modification due to material size reduction. The simple mechanical modification cannot disrupt the internal structure of cellulosic fibers, leading to an insignificant difference of sugar recovery and higher energy input [20]. Therefore, the modification

197 method of freezing NaOH/urea was selected as the efficient pretreatment method in
198 subsequent optimization process.



199

200 **Fig. 2** The effect of different modification methods on enzymatic hydrolysis of textile
201 fibers. Crude textile, freezing NaOH/urea pretreated textile and milling samples were
202 subjected to enzymatic hydrolysis for 72 h at 3% of substrate loadings with 30 FPU/g
203 cellulase and 300 U/g β-glucosidase.

204 3.2 Optimization of sugar recovery from textile waste

205 3.2.1 Different substrate loadings

206 The enzymatic hydrolysis efficiency of cellulose highly depends on temperature, pH,
207 substrate loadings, enzyme dosages and the structural features of substrate [21].
208 Blended textile fabrics are insoluble substrate and thus textile waste hydrolysis was in

209 a heterogeneous system, which led to several difficulties in bioconversion process,
210 such as sufficient mixing. Water content is directly related to the extent of mixing and
211 viscosity of hydrolysis slurry, which has huge influence on the interaction between
212 textile fabrics and enzymes, and thus it affects conversion to glucose and hydrolysis
213 rate. The optimal substrate-to-liquid ratio is of great importance on bioconversion to
214 fermentable sugars. Firstly, in order to assess the optimal substrate loading, hydrolysis
215 was conducted at different substrate loadings, ranging from 1% to 7%. Fig. 3a shows
216 the hydrolysis yield of the pretreated textile fibers at different substrate loadings with
217 30 FPU/g cellulase and 300 U/g β-glucosidase. Hydrolysis results shown in Fig. 3a
218 indicate that the increase of substrate loading from 1% to 7% reduced the glucose
219 yield at 96 h from 98.5% to 86.1%. Similar results have been reported by Shen et al.
220 using steam-pretreated sweet sorghum bagasse as the substrate [22]. Hydrolysis rates
221 at different substrate loadings kept at the same level in the period of 0 h to 24 h (Fig.
222 3b). After 96h, hydrolysis yield of 3%, 5% and 7% substrate loadings decreased by 0%
223 ($p > 0.05$), 5.5% ($p < 0.05$) and 12.4% ($p < 0.05$), respectively as compared with 1%
224 substrate loading. A significant reduction was observed at substrate loadings over 5%,
225 based on the ANOVA analysis. These results suggest that increasing substrate loading
226 had a negative effect on the conversion of cellulose to glucose. This could be
227 explained by the significant product inhibitory effect. As shown in Fig. 3b, higher
228 glucose concentration was obtained when increasing substrate loading rate from 1%
229 to 7%. Over 3% substrate loading ratio, the released glucose in the solution started to
230 limit the cellulase activity during hydrolysis process. This is because glucose has a

strong inhibitory effect on hydrolytic reaction [23]. Kristensen and his coworkers also investigated the relationship between initial substrate loading and the amount of enzyme absorbed, and they found that there was a linear correlation between those two variables [24]. Significant reduction of enzyme adsorption was observed with the increase of initial solid content. As enzyme adsorption is crucial to hydrolysis of insoluble substrates [24], this led to lower glucose recovery yield at higher substrate loadings (5% and 7%). Another possible reason is that the free water content decreased with increasing substrate loading, which limited enzyme transport in buffer solution, and thus led to the reduction of final glucose yield. Furthermore, the remaining cotton content left in recovered polyester increased significantly when substrate loading ratio over 3%, up to 14%, which could result in unsuccessful re-spinning process since cotton could not be melted during melt spinning process. Therefore, in order to digest cotton as much as possible, it could be concluded that the optimal substrate loading was 3% based on the hydrolysis rate and the final glucose yield.

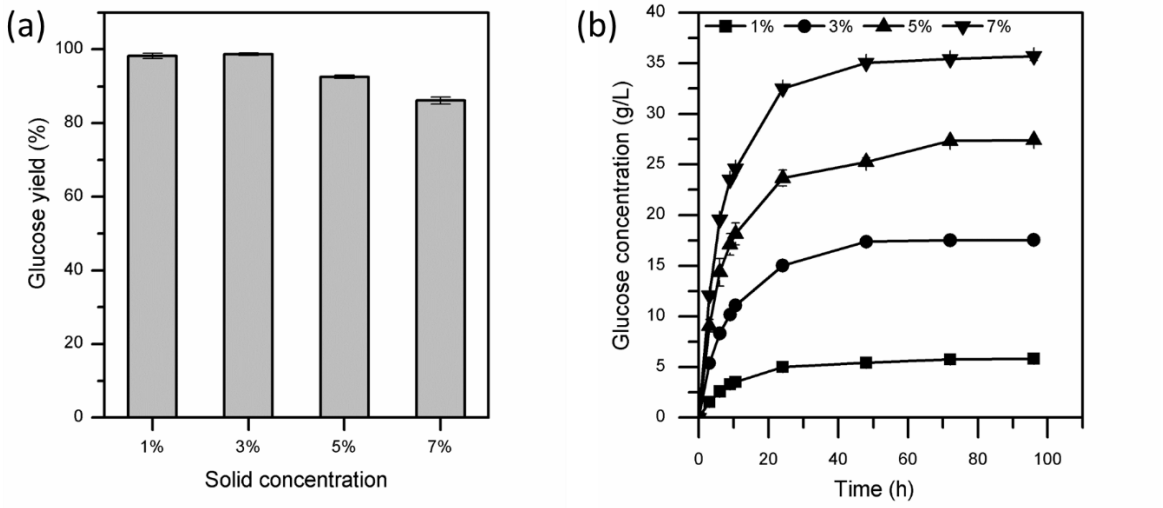


Fig. 3 Enzymatic hydrolysis of pretreated textile fibers at different substrate loadings, a) glucose yield; b) glucose concentration. Freezing NaOH/urea pretreated textile was subjected to enzymatic hydrolysis for 96 h at various substrate loadings (1-7%) with 30 FPU/g cellulase and 300 U/g β-glucosidase.

3.2.2 Temperature and pH

Temperature is a key factor of enzymatic hydrolysis. The optimal incubation temperature is necessary to reduce energy input and to recover the highest amount of glucose from textile waste. Therefore, different temperatures, ranging from 40 ºC to 65 ºC, were investigated at 3% substrate loading with 30 FPU/g cellulase and 300 U/g β-glucosidase. After 96 h, the final glucose yields at different temperatures were shown in Fig. 4. It was found that higher glucose yields were obtained at 45 ºC - 55 ºC and there was no significant difference ($p > 0.05$) in glucose recovery yield under these conditions. The maximum glucose yield of 98.5% was achieved at 50 ºC. It could be noted that higher temperatures over 60 ºC inhibited the conversion from cellulose to glucose. The significant inhibitory effect was observed at 60 ºC ($p < 0.05$) and 65 ºC ($p < 0.05$). The sharp reduction of glucose yield was found at 65 ºC, from 98.5% to 24.4%. It could be attributed to high temperature affecting the adsorption behavior of cellulose and cellulase [25], and thus it has a huge influence on the bioconversion process of cellulosic fiber. It was reported that there was a positive relationship between cellulosic absorption and saccharification efficiency for temperature below 60 ºC [25]. The enzyme denaturation occurred when temperature rose to over 60 ºC and consequently significant decrease of hydrolysis yield was

obtained at 65 ºC due to loss of enzyme activity. The similar results have been reported in previous study, and more than 90% of enzyme activity was lost after 48 h incubation at 60 ºC [26]. The significant decrease ($p < 0.05$) of glucose yield was also observed at 40 ºC. This finding was in good agreement with that of food and vegetable waste [27]. Based on the above results, it could be concluded that the optimum temperature condition for cellulase and β-glucosidase used was 50 ºC and further increase in temperature can result in significant decrease of glucose conversion yield.

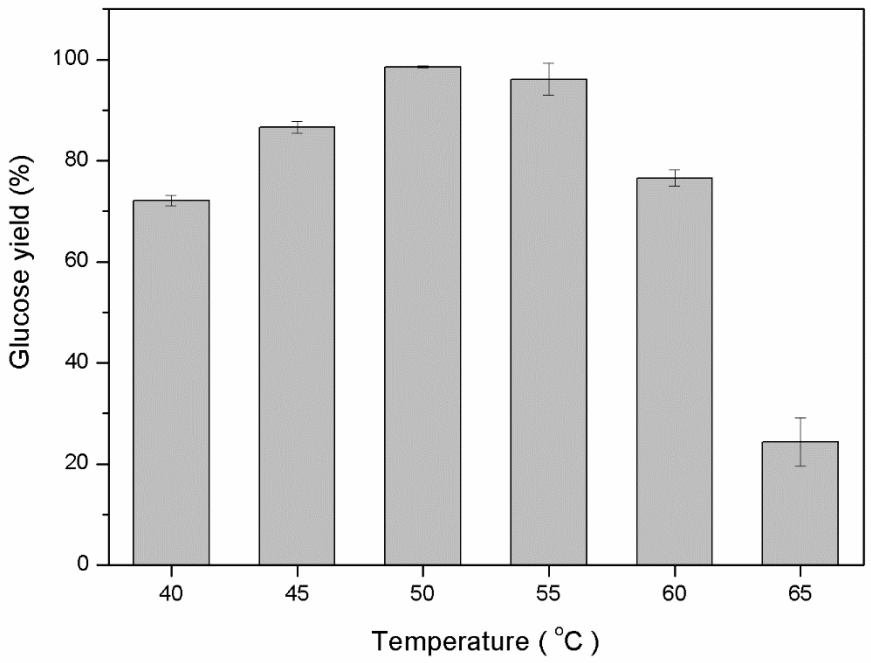


Fig. 4 Glucose yields after 96 h enzymatic hydrolysis of pretreated textile fibers at different temperatures (40-65 ºC). Freezing NaOH/urea pretreated textile was subjected to enzymatic hydrolysis for 96 h at 3% substrate loadings with 30 FPU/g cellulase and 300 U/g β-glucosidase.

282 Hydrolysis pH is one of essential physical parameters influencing glucose conversion
283 yield, since it can affect the cellulase absorption behavior as well [25]. Cellulase
284 produced from different strains has maximum absorption behavior at optimal pH
285 values. Therefore, a range of pH from 4 to 7 was investigated to optimize the
286 hydrolysis condition. After 96 h enzymatic hydrolysis, the glucose yield obtained
287 from pretreated textile fibers were 98.6%, 98.6%, 92.7% and 11.0%, respectively, as
288 presented in Fig. 5. The highest amount of glucose was recovered from cotton fibers
289 at pH 5. Significant reduction of glucose yield was observed when pH rose to 6. The
290 lowest glucose recovery yield was obtained at pH 7, only 11.0%. Recent study
291 conducted by our group reported that the highest amount of glucose was produced
292 from fruit and vegetable waste at pH 5, which was also beneficial for the subsequent
293 fermentation process due to reduction in operation cost on pH adjustment [27].
294 Therefore, hydrolysis pH 5 was selected as the optimal condition.

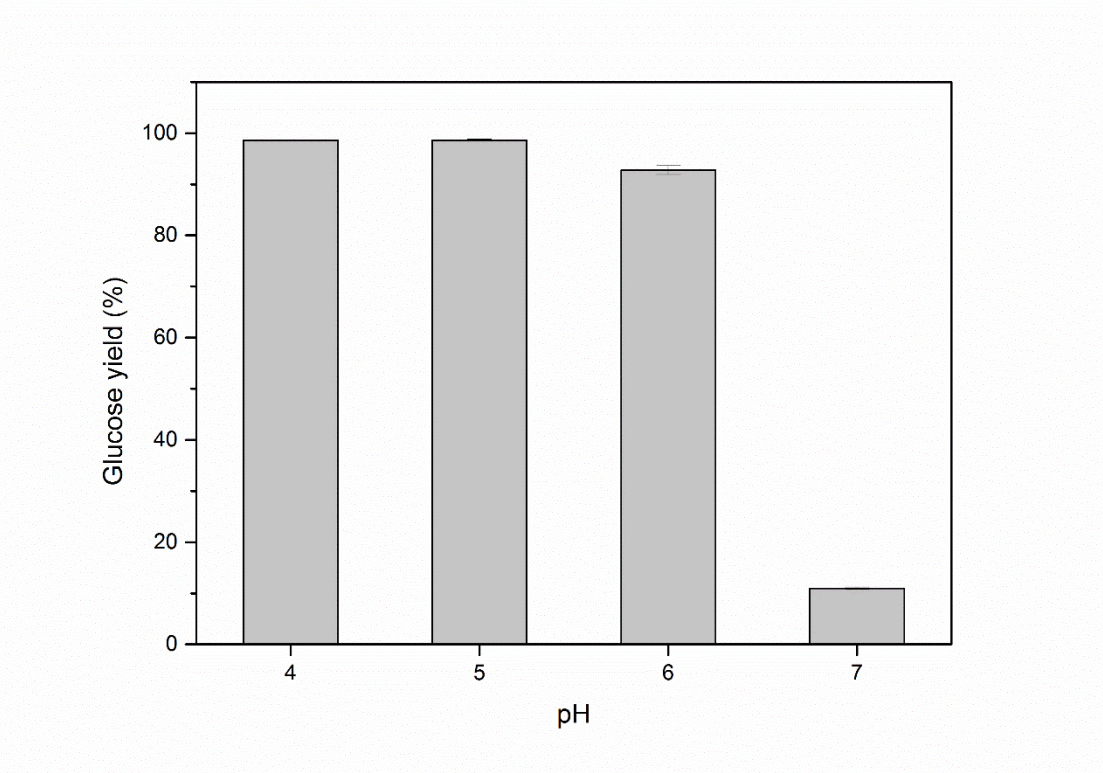


Fig. 5 Glucose yields after 96 h enzymatic hydrolysis of pretreated textile fibers at different pH. Freezing NaOH/urea pretreated textile was subjected to enzymatic hydrolysis for 96 h at 3% substrate loadings with 30 FPU/g cellulase and 300 U/g β-glucosidase.

3.2.3 Cellulase dosage

In order to minimize enzyme input due to high enzyme cost [28], various cellulase dosages ranging from 10 to 40 FPU/g-substrate were investigated at 3% substrate loading ratio for hydrolysis of pretreated textile samples. As presented in Fig. 6, the hydrolysis efficiency was directly related to cellulase dosage, especially at the early stage of hydrolysis. In the early 24 h, the hydrolysis rate and glucose yield improved

along with the increase of cellulase input. It can be attributed to higher ratio of enzymes and substrates, which allows the enzymes to have higher access to textile substrate. After 96 h hydrolysis, the glucose yields obtained with 10, 15, 20, 30 and 40 FPU/g were 69.2%, 83.4%, 89.3%, 91.2% and 91.3%, respectively. Similar glucose yields were obtained at 20, 30 and 40 FPU/g, without significant difference ($p>0.05$). The hydrolysis yield increased significantly by 20.1% ($p < 0.05$) when increasing cellulase dosage from 10 to 20 FPU/g. However, only 2% of enhancement in glucose yield was obtained with further increased cellulase dosage to 40 FPU/g when compared with 20 FPU/g. It could be concluded that the cellulase dosage of 20 FPU/g substrate was selected in subsequent research.

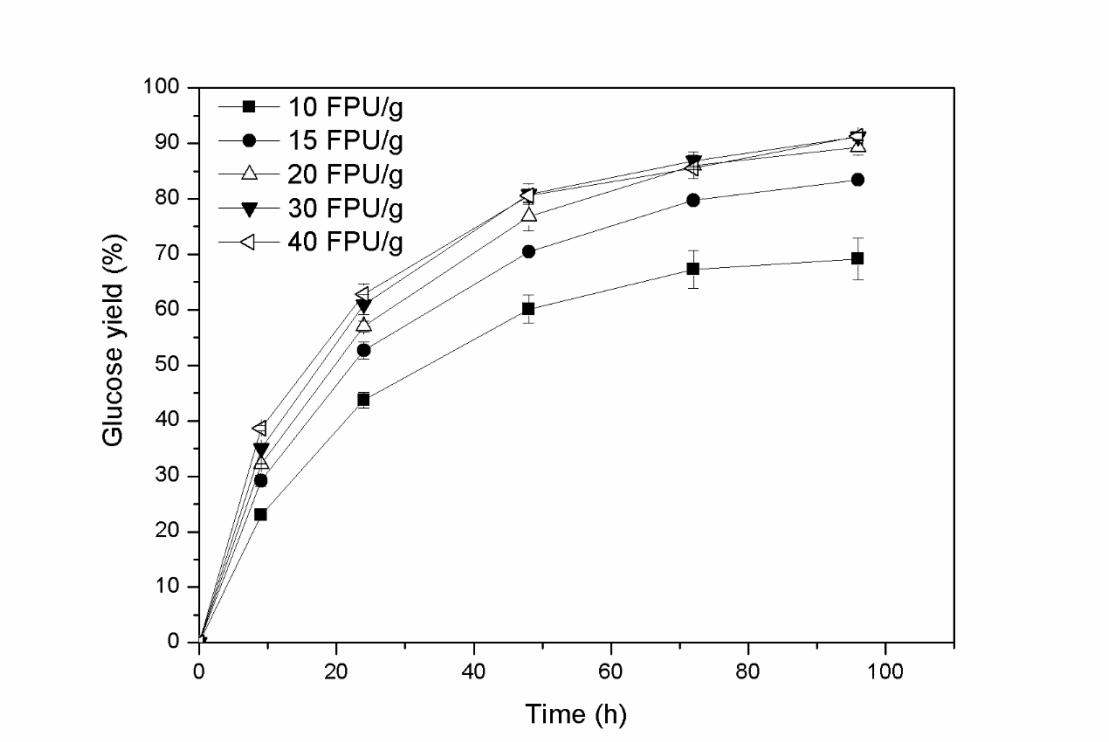


Fig. 6 Enzymatic hydrolysis of pretreated textile fibers at different cellulase dosages. Freezing NaOH/urea pretreated textile was subjected to enzymatic hydrolysis for 96 h

320 at 3% substrate loadings with 10-40 FPU/g cellulase.

321 3.2.4 β-glucosidase supplementation

322 The accumulation of cellobiose was found during hydrolysis process [29] and it was
323 found that cellobiose strongly inhibited cellulase reaction [23,24,29,30], resulting in
324 less effective cellulose hydrolysis to glucose. In order to avoid inhibition of cellobiose,
325 additional β-glucosidase was added to hydrolyze cellobiose to glucose. Determination
326 of the minimum required β-glucosidase input was important to the reduction of
327 hydrolysis cost. Therefore, different β-glucosidase dosages were investigated, ranging
328 from 0 to 50 U/g substrate with the fixed cellulase dosage of 20 FPU/g substrate. As
329 presented in Fig. 7, the sugar recovery yields at 0, 5, 7.5, 10, 20, 30, 40 and 50 U/g
330 β-glucosidase were 87.4%, 92.5%, 96.1%, 98.3%, 98.5%, 98.3%, 98.4% and 98.7%,
331 respectively. Compared with no β-glucosidase supplementation, there was a
332 significant improvement ($p < 0.05$) in hydrolysis yield from 87.4% to 92.5% with the
333 addition of 5 U/g β-glucosidase. The results indicated that the addition of
334 β-glucosidase enhanced glucose yield significantly ($p < 0.05$). The combination of
335 cellulase with β-glucosidase was reported in several investigations [22,25]. Shen et al.
336 found that the glucan-glucose conversion yield increased significantly when
337 β-glucosidase was supplemented during the enzymatic hydrolysis of steam-pretreated
338 sweet sorghum bagasse with SO_2 [22]. Furthermore, results showed that the increase
339 of β-glucosidase dosage from 5 U/g to 10 U/g could improve the hydrolysis yield
340 from 92.5% to 98.3%. It was also noteworthy that further increasing β-glucosidase
341 dosage to over 10 U/g substrate resulted in no improvement of hydrolysis yield to a

higher level ($p > 0.05$). The similar benefits and limitations of the supplementation of β-glucosidase were also observed in previous researches [22,25]. Further increase of β-glucosidase dosage cannot result in any statistical significance and cannot improve the cost-effectiveness of bioconversion to glucose. Therefore, the optimal β-glucosidase dosage was selected as 10 U/g substrate.

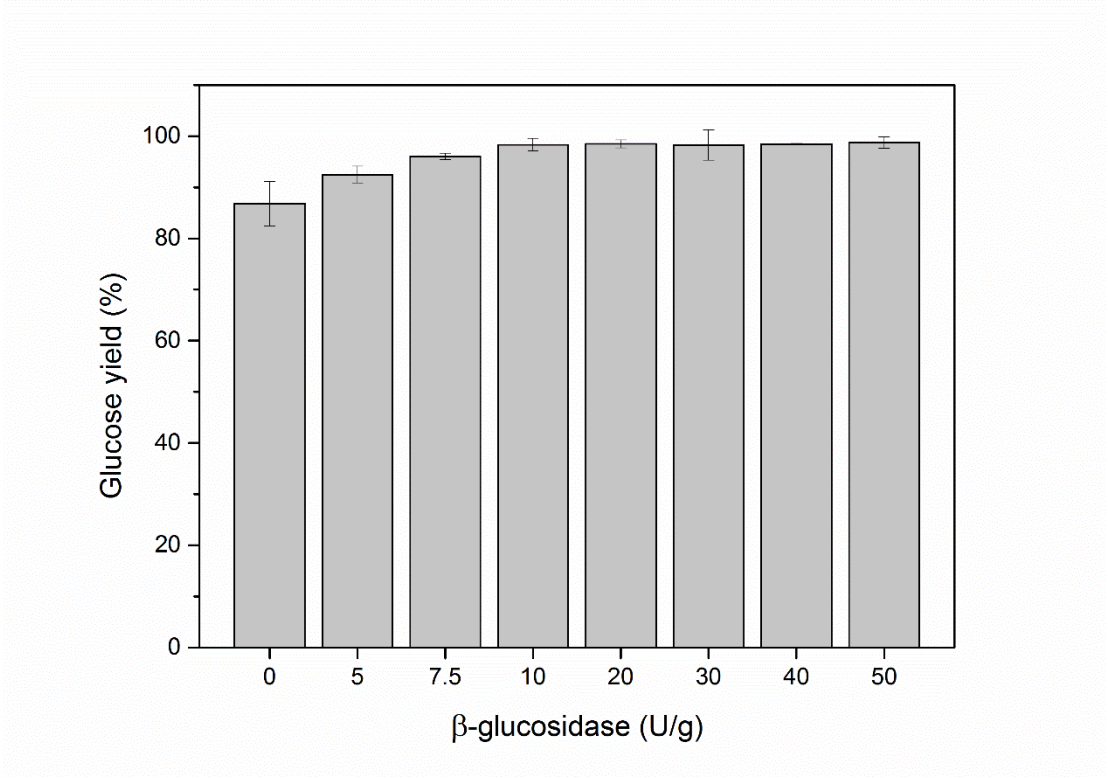


Fig. 7 Glucose yields after 96 h enzymatic hydrolysis of pretreated textile fibers at different β-glucosidase dosages. Freezing NaOH/urea pretreated textile was subjected to enzymatic hydrolysis for 96 h at 3% substrate loadings with 20 FPU/g cellulase and 0-50 U/g β-glucosidase.

Textile waste pretreated by different methods has been conducted by previous studies

354 [2]. The comparison of glucose yield recovered from different modification methods
355 and various enzyme dosages was summarized in Table 1. As compared to results from
356 blended textile, higher glucose yield was obtained from pretreated 100% cotton,
357 reaching 99.1%, whereas the highest glucose yield was 91% from blended cotton/PET
358 fiber. Remarkably, glucose yield obtained from our study is the highest (98.3%) when
359 compared to recovery yield from other blended fibers, and relatively low level of
360 enzyme was consumed, leading to decrease in enzyme cost. Melt spinning is the
361 commonly used method for PET fiber production. The impurities in recovered PET i.e.
362 residual cotton, cannot be melted during re-spinning process and these pose a high
363 risk to the machine because of possible blockage, which affects the quality of re-spun
364 PET fibers. Higher glucose released from textile waste means there are less cotton
365 residues in recovered PET product. Therefore, the highest glucose yield (98.3%) also
366 contributes to the reuse of recovered PET fiber by melt spinning due to lower
367 impurity content.

368 Table 1 Comparison of glucose yield recovered from different pretreatment methods on textile waste

Substrate	Pretreatment	Enzymes	Glucose yield (%)	Reference
white 40/60 polyester/cotton blend	NaOH/urea (7/12 wt%) at -20 ºC for 1h	30 FPU cellulase and 60 U β-glucosidase per gram of cellulose for 72h	91.0	[8]
Cotton liner	12 wt% NaOH at 0 ºC for 3h	20 FPU cellulase and 30 U β-glucosidase per gram of cellulose for 96h	99.1	[11]
Used jeans	85% phosphoric acid at 50 ºC for 7h	7.5 FPU cellulase and 15 CBU β-glucosidase per gram of cellulose for 96h	79.2	[13]
100% cotton linters,	5 g/L $Na_2S_2O_4$ and Na_2CO_3 solution 100 ºC for 1 h and the treated by 85% phosphoric acid 50 ºC, 100 rpm for 2 h	10 FPU cellulase per gram of substrate for 48h	90.0	[31]
red T-shirt			80.0	
blue polyester/cotton (40/60) blended shirt			60.0	
100% cotton T-shirts	[AMIM]Cl (ionic liquid) 110 ºC for 90 min	66 FPU cellulase per gram of substrate for 48h	95.0	[32]
Blue 60/40 polyester/cotton blend	NaOH/urea (7/12 wt%) at -20 ºC for 6h	20 FPU cellulase per gram and 10 U β-glucosidase of substrate for 96 h	98.3	This study

3.3 Changes of surface morphology

The structural change of textile substrate (pretreated cotton/PET 60/40) was observed by optical microscope at the magnification of ×400. The pictures of optical microscope observation were shown in Fig. 8. The broken and disordered cotton fibers were identified clearly in Fig. 8a. The PET fibers were left, and cotton fibers could not be found in remaining fibers as shown in Fig. 8b, which was consistent with the sugar recovery yield obtained from pretreated textiles (98.3%). In order to investigate the changes of surface morphology, textile substrate was subjected to the detection of SEM at the magnification of ×300. According to the SEM images of pretreated cotton/PET 60/40, dramatic changes of surface morphology can be observed on textile after hydrolysis. As presented in Fig. 9a, two types of fibers can be identified. The belt-shaped cotton fibers and the round-shaped polyester fibers were blended in a compact binding structure before enzymatic hydrolysis. After enzymatic hydrolysis (Fig. 9b), the binding was obviously loosed with less fibers. Many small holes among fibers were observed. This is because in enzymatic hydrolysis, most cellulosic fibers were digested to soluble sugars and non-biodegradable PET fibers were left in fabrics. The recovered PET fibers presented a smooth surface with no significant structural change, as presented in Fig. 9b. However, small amount of broken polyester fibers was observed before and after enzymatic hydrolysis, which can be attributed to the alkaline pretreatment. Gholamzad et al. also reported that there was minor change on PET fibers recovered from alkaline pretreated textile waste [8]. The results of FTIR, viscosity analysis and DSC indicated that there was a

minimal effect on the properties of recovered PET fibers [8]. Therefore, these images demonstrated that cotton fibers were converted to glucose and removed from textile waste by enzymatic hydrolysis, while there was no obvious change in shape and macroscopic structure on PET fibers.

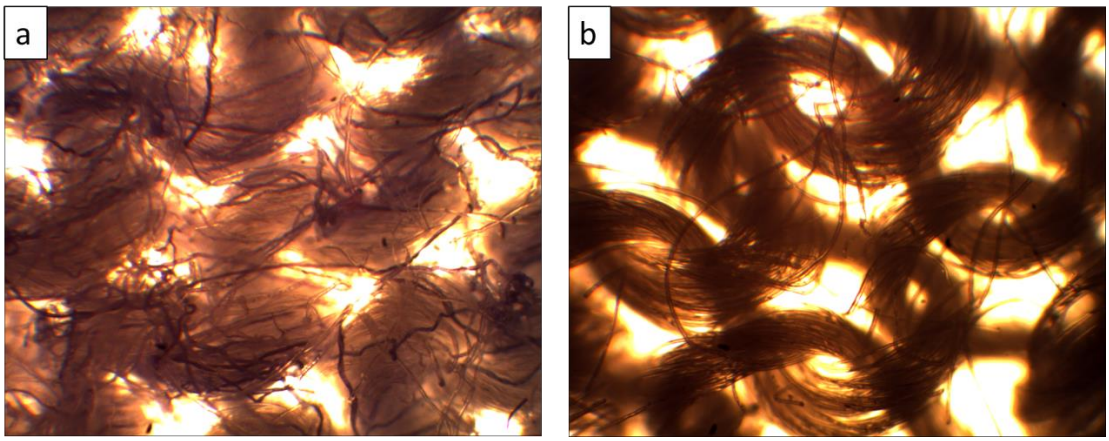


Fig. 8 Optical microscopic pictures of textile substrate (pretreated 60/40) before and after enzymatic hydrolysis (a. pretreated textile substrate before hydrolysis; b. pretreated textile substrate after hydrolysis)

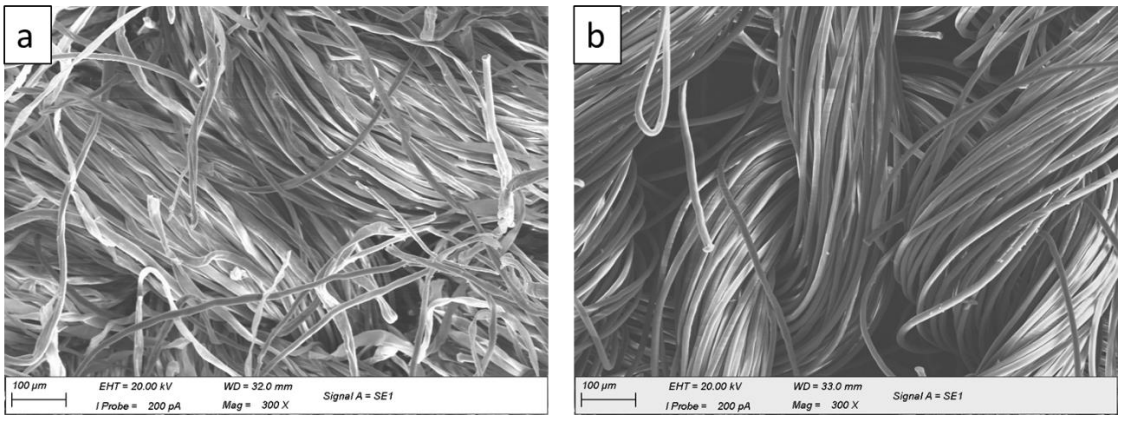


Fig. 9 SEM pictures of textile substrate (pretreated 60/40) before and after enzymatic hydrolysis (a. pretreated textile fibers before hydrolysis at magnification of ×300; b. pretreated textile fibers after hydrolysis at magnification of ×300)

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3.4 Future perspective of PET recycling

Currently, the raw materials to produce PET fibers are monoethylene glycol and purified terephthalic acid obtained from crude oil refinery process. It is estimated that 70 million barrels of oil is used for polyester fiber per year [33]. It is noteworthy that the traditional PET production process is energy-intensive and highly relies on non-renewable fossil fuels. Based on our textile waste recycling process, recovered polyester from textile wastes were obtained after enzymatic hydrolysis, which provides a clean and sustainable way of PET separation. It was reported that 33%-53% less energy was used to recycle polyester as compared with virgin polyester production. Moreover, 54% reduction in carbon dioxide emission was resulted during PET recycling [33]. Therefore, the recycling of PET fibers deserves significant attention and considerable efforts in further investigation. In our group, the recovered PET from textile waste fiber has been re-spun into new fibers by melt spinning and upscaling valorization of textile waste through biological treatment are currently under investigation. The technical and economic feasibility for industrial application will be demonstrated in the future.

4 Conclusions

Recovery of glucose and polyester from textile waste through enzymatic hydrolysis was investigated in this study. Proper modification method was selected at first. Substrate loading, temperature, cellulase dosage and β-glucosidase dosage were optimized to reduce the hydrolysis cost. The maximum glucose recovery of 98.3%

was obtained with 20 FPU/g of cellulase dosage and 10 U/g of β-glucosidase dosage at 3% (w/v) substrate loading, temperature of 50 °C and pH 5. In conclusion, a bioconversion process using textile wastes to recover glucose and PET with low enzyme input has been successfully developed in this study.

Acknowledgements

The authors give appreciation to the Hong Kong Research Institute of Textiles and Apparel (HKRITA) and the Innovation and Technology Commission (ITC) in Hong Kong for the Innovation and Technology Fund (ITP/109/15TP). The authors also express gratitude to the industrial sponsors H&M Conscious Foundation and H&M (Far East) Ltd. Sincere appreciation to Dr. Shao-Yuan Leu (The Hong Kong Polytechnic University) and Dr. Hao Liu (South China University of Technology, China) for providing kind assistance on pretreatment.

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